

# Thermodynamic Functions and Properties of MgO at High Compression and High Temperature

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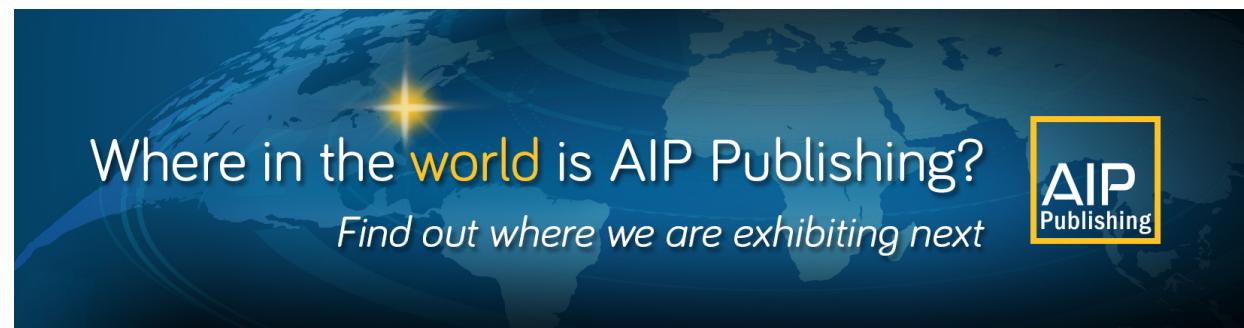
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# Thermodynamic Functions and Properties of MgO at High Compression and High Temperature

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The complete thermodynamic functions for MgO are presented for the temperature range 300–2000 K and the pressure range 0–150 GPa, both as tables and as graphs. Careful attention is given to the temperature and pressure dependence of the coefficient of thermal expansion  $\alpha$  and the isothermal bulk modulus  $K_T$ , which are the major corrections to the thermodynamic functions in extreme conditions. Our equations efficiently use the fact that the product  $\alpha K_T$  varies only slightly with either temperature or with volume, although scrupulous care is taken to account for the actual numbers. The corrections are now possible due to recent measurements of the bulk modulus up to 1800 K. The Birch–Murnaghan equation of state is used to account for certain terms in the expressions for internal energy and enthalpy. The parameters used in the Birch–Murnaghan equation of state are given as functions of temperature. The parameters which presently limit the calculations of thermodynamic functions to even higher temperatures and pressures and limit the applications of this method to other minerals are: (1) the uncertainty of the thermal expansivity at temperatures above 1500 K, and (2) the uncertainty of the temperature dependence of  $(\partial K_T / \partial T)_P$  at temperatures above 800 K.

Key words: thermodynamic functions; high-temperature properties; mineral physics; entropy of MgO; Gibbs energy of MgO; Helmholtz energy of MgO.

## Contents

1. Introduction .....	70	6. Appendix: Derivation of Equations in the Main Text .....	82
2. Thermodynamic Functions for MgO .....	70	6.1. Derivation of Equation (1) .....	82
2.1. Entropy Versus Volume and Temperature .....	70	6.2. Derivation of Equation (6) .....	82
2.2. Internal Energy Versus Volume and Temperature .....	71	6.3. Derivation of Equation (11) .....	82
2.3. The Helmholtz Energy Versus Volume and Temperature .....	73	6.4. Derivation of Equation (15) .....	83
2.4. Entropy Versus Pressure and Temperature .....	73		
2.5. Enthalpy Versus Pressure and Temperature .....	74		
2.6. The Gibbs Energy Versus Pressure and Temperature .....	73		
2.7. Evidence for the Quasiharmonic Model for MgO out to 2000 K .....	73		
3. The Strategy of the Calculations .....	74		
3.1. Zero Pressure Data .....	77	1. Laboratory input data .....	71
3.2. Compression Data at Absolute Zero .....	78	2. Thermodynamic data calculated from Table 1 ..	71
3.3. The Original Experimental Data and Probable Errors .....	78	3. Entropy versus $T$ at constant $\chi$ , $S(T, V/V_0)$ .....	72
4. Acknowledgments .....	79	4. Entropy versus $\chi$ at constant $T$ , $S(V/V_0, T)$ .....	73
5. References .....	81	5. Internal energy versus $T$ at constant $\chi$ , $U(T, V/V_0)$ .....	73
	81	6. Helmholtz energy versus $\chi$ at constant $T$ , $F(V/V_0, T)$ .....	74
	81	7. Helmholtz energy versus $T$ at constant $\chi$ , $F(T, V/V_0)$ .....	76
	82	8. Entropy versus $T$ at constant $P$ , $S(T, P)$ .....	76
	82	9. Enthalpy versus $T$ at constant $P$ , $H(T, P)$ .....	77
	82	10. Enthalpy versus $P$ at constant $T$ , $H(P, T)$ .....	77
	82	11. The Gibbs energy versus $T$ at constant $P$ , $G(T, P)$ .....	79

## List of Tables

1. Laboratory input data .....	71
2. Thermodynamic data calculated from Table 1 ..	71
3. Entropy versus $T$ at constant $\chi$ , $S(T, V/V_0)$ .....	72
4. Entropy versus $\chi$ at constant $T$ , $S(V/V_0, T)$ .....	73
5. Internal energy versus $T$ at constant $\chi$ , $U(T, V/V_0)$ .....	73
6. Helmholtz energy versus $\chi$ at constant $T$ , $F(V/V_0, T)$ .....	74
7. Helmholtz energy versus $T$ at constant $\chi$ , $F(T, V/V_0)$ .....	76
8. Entropy versus $T$ at constant $P$ , $S(T, P)$ .....	76
9. Enthalpy versus $T$ at constant $P$ , $H(T, P)$ .....	77
10. Enthalpy versus $P$ at constant $T$ , $H(P, T)$ .....	77
11. The Gibbs energy versus $T$ at constant $P$ , $G(T, P)$ .....	79

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12. The pressure and the function $\int P d(V/V_0)$ versus $\chi$ .....	80	4. The isothermal plots of Helmholtz energy, $F_T$ , versus $\chi$ .....	75
13. The compression, $\chi = V/V_0$ , and the functions $\int \chi dP$ and $\int P d\chi$ versus $P$ .....	80	5. The isobaric plots of entropy, $S_P$ , at constant $P$ versus $T$ .....	77
		6. The isobaric plots of enthalpy, $H_P$ , at constant $P$ versus $T$ .....	78
		7. The isothermal plots of enthalpy, $H_P$ , at constant $T$ versus $P$ .....	78
		8. The isobaric plots of Gibbs energy, $G$ , at constant $P$ versus $T$ .....	79
		9. Comparison of entropy at constant $P$ and constant $\chi$ versus $T$ and the comparison of $C_P$ and $C_V$ versus $T$ .....	80
		10. The volume thermal expansivity of $Mg_2SiO_4$ versus $T$ .....	81

### List of Figures

1. The isochoric plots of entropy, at constant $V/V_0$ , versus $T$ .....	72
2. The isochoric plots of internal energy, $U_\chi$ , versus $T$ .....	74
3. The isochoric plots of Helmholtz energy, $F_\chi$ , versus $T$ .....	75

## 1. Introduction

The principal objective of this work is to evaluate and publish the data for all the thermodynamic functions of an important mineral, MgO or periclase, with a temperature range of 300 to 2000 K, and with a compression range of  $V/V_0 = 1$  to  $V/V_0 = 0.7$  (corresponding to  $P = 150$  GPa).

It is well known that the computations of thermodynamic functions (entropy, for example) require knowledge of the thermal expansivity  $\alpha$  and compressibility  $\kappa$  as well as the specific heat. The pressure (or volume) and temperature variation of  $\alpha$  and  $\kappa$  contribute to the pressure (or volume) and temperature variation of the thermodynamic functions. The tabulation of these thermodynamic functions in the extreme ranges of temperature and pressure requires a good understanding of the equation of state, elasticity at very high temperature, anharmonicity of the solid, and the thermal expansivity at high temperature.

Recent experimental progress in the thermal equation of state has clarified the volume and high-temperature corrections to the thermal pressure,  $P_{TH}$  and to the isothermal bulk modulus  $K_T$  (the reciprocal of the compressibility  $\kappa$ ), for MgO.<sup>1</sup> This progress is represented by the ability to measure elastic constants at high temperatures (in fact as high as 1825 K) using new resonance measurement techniques.<sup>2,3</sup>

It has become apparent from this recent research that it is best to treat  $\alpha K_T$  as a single parameter, since the product varies little with volume or temperature, whereas both  $\alpha$  and  $K_T$  each vary significantly with volume and with temperature. The physical significance of the single parameter  $\alpha K_T$  is that it is identical to the important function  $(\partial P/\partial T)_V$ .

A preliminary publication on a few graphs of the thermodynamic functions as well as the complete derivation of the basic equations have been presented elsewhere.<sup>4</sup> The graphs and tables presented here are a complete set, and are based upon published data.<sup>5-7</sup>

The molecular weight of MgO is taken to be 40.3114, and the conversion between calories and joules is taken to be 4.1855 J/cal.<sup>8</sup> We make much use of the conversion between pressure and energy density: 1 GPa =  $10^3$  J/ml.

The important input thermodynamic data on MgO are given in Table 1: The adiabatic bulk modulus  $K_S$  is taken from the experiments of Sumino *et al.*<sup>5</sup> with the values at

higher  $T$  coming from Isaak *et al.*<sup>9</sup>; the data on the coefficient of thermal expansion  $\alpha$  are from Suzuki *et al.*<sup>6</sup>; and the data on specific heat,  $C_P$ , are from the "CODATA" thermodynamic tables of Garvin *et al.*<sup>7</sup> Table 1 gives  $\alpha$ , the density  $\rho$ ,  $K_S$ , and  $C_P$ , all at constant pressure  $P = 0$ , and as functions of  $T$  up to 2000 K. In this table, we also present the value of the Grüneisen parameter,  $\gamma$  vs  $T$  at constant  $P = 0$  computed from  $\gamma = \alpha K_S / (\rho C_P)$ , and the resultant specific heat versus  $T$  at constant  $V$ ,  $C_V$ , computed from  $C_P/C_V = 1 + \alpha\gamma T$ . Table 1 constitutes the basic thermodynamic data. From these data we list in Table 2 the following calculated fundamental thermodynamic parameters versus  $T$  at  $P = 0$ : the isothermal bulk modulus  $K_T$  where  $K_S/K_T = 1 + \alpha\gamma T$ ;  $\alpha K_T$ ;  $(\partial K_T/\partial T)_P$ ; the computed isochoric temperature derivative of  $K_T$ ,  $(\partial K_T/\partial T)_V$ ; and the thermal pressure  $P_{TH}$  where

$$P_{TH}(T) - P_{TH}(T_0) = \int_{T_0}^T \alpha K_T dT.$$

The equation relating  $(\partial K_T/\partial T)_V$  to input parameters is shown in the Appendix [Eqs. (A4) and (A5) and discussion following Eq. (18)].

## 2. Thermodynamic Functions of MgO

### 2.1. Entropy Versus Volume and Temperature

The change of entropy with volume from  $V_0$  to  $V$ , or  $\chi = V/V_0$  from 1 to  $V/V_0$ , along an isotherm  $T^*$  is given by (see Appendix, Sec. 6.1.)

$$\begin{aligned} S(T^*, \chi) - S(T^*, 1) &= -(\alpha K_T)_{T^*} V_0 \left( 1 - \frac{V}{V_0} \right) \\ &\quad + w V_0 \left( \frac{V}{V_0} \ln \frac{V_0}{V} + \frac{V}{V_0} - 1 \right) \\ &= -(\alpha K_T)_{T^*} \left( \frac{1}{\rho_0} \right) (1 - \chi) \\ &\quad + w \left( \frac{1}{\rho_0} \right) \left( \chi \ln \frac{1}{\chi} + \chi - 1 \right), \end{aligned} \quad (1)$$

where  $\rho_0$  = zero pressure density at  $T^*$ . The reference volume  $V_0$  is taken at  $P = 0$  and  $T = 300$  K. The parameter

$$w = (\partial K_T/\partial T)_V \quad (2)$$



Table 3. Entropy vs.  $T$  at constant  $\chi$ ,  $S(T, V/V_0)$ 

$T$ (K)	$S(T, 1.0)$	$S(T, 0.95)$	$S(T, 0.90)$	$S(T, 0.85)$ (J g <sup>-1</sup> K <sup>-1</sup> )	$S(T, 0.80)$	$S(T, 0.75)$	$S(T, 0.70)$
300	0.6705	0.60	0.53	0.46	0.39	0.33	0.26
350	0.817	0.74	0.66	0.59	0.51	0.43	0.35
400	0.953	0.87	0.79	0.72	0.64	0.56	0.48
450	1.077	1.00	0.91	0.83	0.75	0.67	0.59
500	1.192	1.11	1.02	0.94	0.86	0.78	0.69
550	1.297	1.21	1.13	1.04	0.96	0.87	0.79
600	1.395	1.31	1.22	1.14	1.05	0.97	0.88
650	1.486	1.40	1.31	1.23	1.14	1.05	0.97
700	1.571	1.48	1.40	1.31	1.22	1.13	1.05
750	1.651	1.56	1.47	1.39	1.30	1.21	1.13
800	1.736	1.64	1.55	1.46	1.37	1.29	1.20
850	1.797	1.71	1.62	1.53	1.44	1.35	1.27
900	1.864	1.77	1.68	1.59	1.51	1.42	1.33
950	1.928	1.84	1.75	1.66	1.57	1.48	1.39
1000	1.988	1.90	1.81	1.72	1.63	1.54	1.45
1050	2.046	1.96	1.87	1.78	1.69	1.60	1.51
1100	2.101	2.01	1.92	1.83	1.74	1.65	1.57
1150	2.154	2.06	1.97	1.88	1.80	1.71	1.62
1200	2.204	2.11	2.02	1.93	1.84	1.76	1.67
1250	2.254	2.16	2.07	1.98	1.90	1.81	1.72
1300	2.299	2.21	2.12	2.03	1.94	1.85	1.77
1350	2.344	2.25	2.16	2.07	1.99	1.90	1.81
1400	2.387	2.30	2.21	2.12	2.03	1.94	1.86
1450	2.429	2.34	2.25	2.16	2.07	1.98	1.90
1500	2.470	2.38	2.29	2.20	2.11	2.03	1.94
1550	2.509	2.42	2.33	2.24	2.15	2.07	1.98
1600	2.546	2.46	2.37	2.28	2.19	2.10	2.02
1650	2.583	2.49	2.40	2.32	2.23	2.14	2.05
1700	2.619	2.53	2.44	2.35	2.27	2.18	2.09
1750	2.653	2.56	2.48	2.39	2.30	2.21	2.13
1800	2.687	2.60	2.51	2.42	2.33	2.25	2.16
1850	2.720	2.63	2.54	2.45	2.37	2.28	2.19
1900	2.751	2.66	2.57	2.49	2.40	2.31	2.22
1950	2.782	2.69	2.60	2.52	2.43	2.34	2.25
2000	2.813	2.72	2.63	2.55	2.46	2.37	2.28

$$\begin{aligned}
 U(T^*, \chi) - U(T^*, 1) \\
 = (T^* \Delta S_\chi)_{T^*} - P_{TH}(1/\rho_0)(0.988 - \chi) - \int P_0 dV,
 \end{aligned}
 \quad (6)$$

(see Appendix). We see that the equation of state becomes important to  $U$  through the term  $\int P_0 dV$ . Here  $\rho_0$  refers to the zero pressure value appropriate to the isotherm  $T^*$ . For  $P_0$  (along the isotherm  $T=0$ ), we use the Birch-Murnaghan equation of state of the third degree.<sup>11</sup>

$$\begin{aligned}
 P_0 = P\left(\frac{\rho}{\rho_0}\right) = \frac{3}{2} K_0 (y^{7/3} - y^{5/3}) \\
 \times \left[ 1 + \frac{3(K'_0 - 4)(y^{2/3} - 1)}{4} \right],
 \end{aligned}
 \quad (7)$$

where  $y = \rho/\rho_0$ ,  $\rho_0$  is the absolute zero density at  $P=0$ , so that for  $\rho_0$  in Eq. (7) we have 3.6312 g/ml. In the integration of  $P_0$ , there arises a dimensionless expression multiplied by the term  $K_0 V_{00}$ , which is also  $K_0/\rho_0 = 166.2/3.6312$  GPa g<sup>-1</sup> ml<sup>-1</sup> = 4.577 × 10<sup>4</sup> J/g.

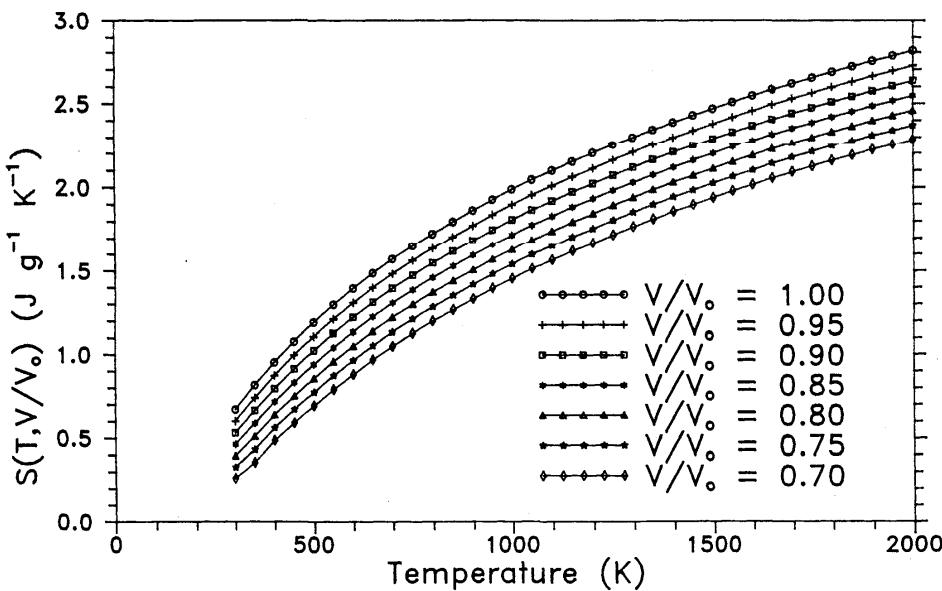
FIG 1 The isochoric plots of entropy, at constant  $V/V_0$ , vs  $T$

Table 4. Entropy vs.  $\chi$  at constant  $T$ ,  $S(V/V_0)$ 

$x-V/V_0$	$S(x,300)$	$S(x,500)$	$S(x,1000)$	$S(x,1500)$	$S(x,2000)$
0.70	0.260	0.69	1.45	1.94	2.28
0.72	0.286	0.73	1.49	1.97	2.32
0.74	0.313	0.76	1.52	2.01	2.35
0.76	0.340	0.79	1.56	2.04	2.39
0.78	0.367	0.82	1.59	2.08	2.42
0.80	0.394	0.86	1.63	2.11	2.46
0.82	0.421	0.89	1.66	2.15	2.49
0.84	0.449	0.92	1.70	2.18	2.53
0.86	0.476	0.96	1.74	2.22	2.56
0.88	0.503	0.99	1.77	2.25	2.60
0.90	0.531	1.02	1.81	2.29	2.63
0.92	0.559	1.06	1.84	2.33	2.67
0.94	0.587	1.09	1.88	2.36	2.71
0.96	0.614	1.12	1.92	2.40	2.74
0.98	0.642	1.16	1.95	2.43	2.78
1.00	0.6705	1.19	1.99	2.47	2.81
1.02	0.699	1.23	2.02	2.51	2.85
1.04	0.727	1.26	2.06	2.54	2.88
1.06	0.755	1.29	2.10	2.58	2.92
1.08	0.784	1.33	2.13	2.61	2.96
1.10	0.812	1.36	2.17	2.65	2.99
1.12	0.841	1.39	2.21	2.69	3.03
1.14	0.870	1.43	2.24	2.72	3.06
1.16	0.898	1.46	2.28	2.76	3.10
1.18	0.927	1.50	2.32	2.80	3.14

The variation of internal energy  $U$  with temperature at  $\chi = 1$  above  $T = 300$  K is given by

$$U(T^*, 1) - U(300, 1) = \int_{300}^{T^*} C_V dT. \quad (8)$$

We need the value of  $U(300, 1)$ , which is obtained, for example, by integrating the values of  $C_P - C_V$ , as tabulated by Barron *et al.*,<sup>10</sup> up to 300 K, or by computing the thermal pressure effect on the enthalpy (see Appendix, Sec. 6.4.). We find

$$U(300, \chi = 1) = 127.3 \text{ J/g for MgO}. \quad (9)$$

One further explanation needs to be made for Eq. (7). This equation is in fact valid only at absolute zero. The value of  $\rho_0$  for MgO at 0 K is 3.6312, compared with  $\rho(300, P = 0) = 3.587$ . In the calculations of the functions, we use  $\rho_0 = 3.5877$  since our standard state is at 300 K. Properties at temperatures below 300° correspond to values of  $\chi$  less than unity at  $P = 0$  ( $\chi = 0.988$  at  $T = 0$ ).

Equations (6) and (7) were used to calculate  $U$  vs  $\chi$  and  $T$ , and the values are listed in Table 5 and plotted in Fig. 2.

### 2.3. The Helmholtz Energy Versus Volume and Temperature

The Helmholtz energy is given by

$$F = U - TS. \quad (10)$$

Calculating  $F$  is straightforward. The tabulated results of  $F$  vs  $\chi$  at constant  $T$  are given in Table 6. A plot of  $F_\chi$  vs  $T$  for MgO is shown in Fig. 3, and a plot of  $F_T$  vs  $\chi$  for MgO is shown in Fig. 4. Table 7 shows the Helmholtz energy versus  $T$  at constant  $\chi$ .

The minimum of  $F(T, V/V_0)$  locates the specific volume at  $T$ . We see from Fig. 4 that the minimum increases as  $T$  increases, and this will obey the law  $dV/V = \alpha dT$ .

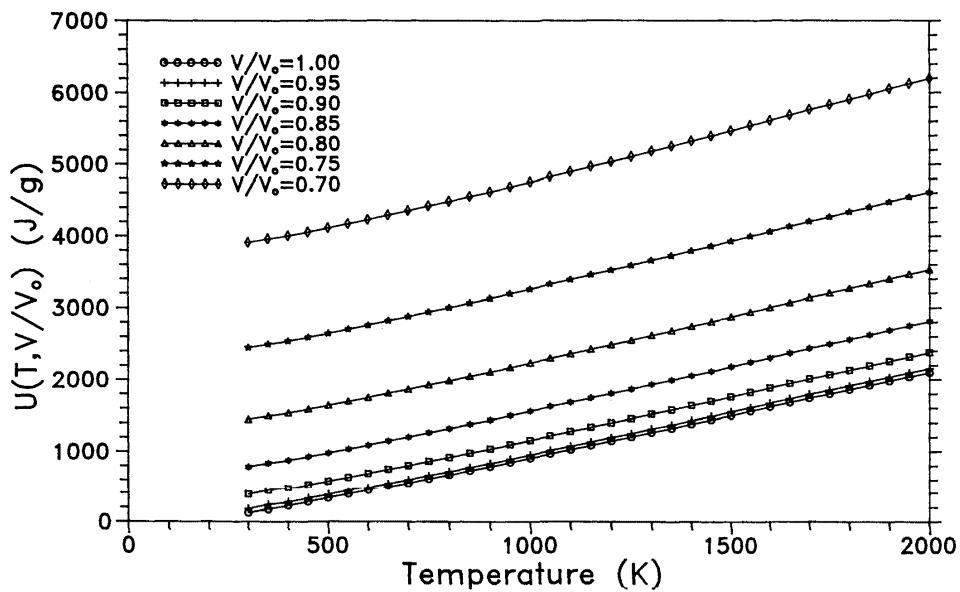
### 2.4. Entropy Versus Pressure and Temperature

The values of the constant pressure entropy,  $S_P$  vs.  $T$  at  $P = 0$ ,  $S_P(T, 0)$  are taken from Garvin *et al.*,<sup>7</sup> and found in the first column of Table 8. The values of entropy versus  $P$

Table 5. Internal energy vs.  $T$  at constant  $\chi$ ,  $U(T, V/V_0)$ 

$T$ (K)	$U(T, 1.0)$	$U(T, 0.95)$	$U(T, 0.90)$	$U(T, 0.85)$	$U(T, 0.80)$	$U(T, 0.75)$	$U(T, 0.70)$
300	127.3	180	380	790	1440	2450	3910
350	175.0	240	440	840	1500	2490	3960
400	225.7	280	480	880	1540	2540	4000
450	278.5	330	530	930	1590	2590	4050
500	332.8	380	580	980	1640	2640	4110
550	388.3	440	640	1040	1700	2700	4170
600	444.5	490	690	1090	1750	2760	4230
650	501.4	550	750	1150	1810	2820	4290
700	558.8	610	810	1210	1870	2880	4360
750	616.6	660	860	1260	1930	2940	4420
800	674.7	720	920	1320	1990	3000	4490
850	733.1	780	980	1380	2050	3070	4550
900	791.8	840	1040	1440	2110	3130	4620
950	850.7	900	1100	1500	2170	3190	4690
1000	909.7	960	1160	1560	2230	3260	4750
1050	968.8	1020	1220	1620	2300	3330	4830
1100	1028.1	1070	1280	1690	2360	3390	4890
1150	1087.4	1130	1340	1750	2430	3460	4970
1200	1146.7	1190	1400	1810	2490	3520	5030
1250	1206.1	1250	1460	1870	2550	3590	5110
1300	1265.6	1310	1520	1930	2620	3660	5180
1350	1325.0	1370	1580	2000	2680	3730	5250
1400	1384.5	1430	1640	2060	2750	3800	5320
1450	1444.1	1490	1700	2120	2810	3860	5390
1500	1503.6	1550	1770	2180	2880	3930	5470
1550	1563.2	1620	1830	2250	2940	4000	5540
1600	1622.8	1670	1890	2310	3010	4070	5610
1650	1682.4	1740	1950	2370	3070	4140	5690
1700	1742.0	1800	2010	2440	3140	4210	5760
1750	1801.6	1860	2070	2500	3200	4270	5830
1800	1861.2	1920	2130	2560	3270	4340	5910
1850	1920.9	1980	2200	2620	3330	4410	5980
1900	1980.5	2040	2260	2690	3400	4480	6050
1950	2040.2	2100	2320	2750	3460	4550	6120
2000	2099.9	2160	2380	2810	3530	4620	6200

$V_0$  is standard volume at  $T = 300$  K and  $P = 1$  atmosphere.

FIG. 2. The isochoric plots of internal energy  $U_v$  vs  $T$ .

along the isotherm  $T^*$  are found to be (see Appendix)

$$\begin{aligned} S_p(T^*, P) - S_p(T^*, 0) = & -(\alpha K_T)_{T^*}(1/\rho_0)(1 - \chi_0) \\ & - K_V(T^*, 0)(1/\rho_0) \\ & \times (\chi_0 \ln \chi_0 + 1 - \chi_0), \end{aligned} \quad (11)$$

where

$$\rho_0 = \rho(T^*, P = 0)$$

and

$$\chi_0 = \frac{V(T^*, P)}{V(T^*, P = 0)}. \quad (12)$$

$V(T^*, P = 0)$  is found by integrating the coefficient of thermal expansivity:

Table 6. Helmholtz energy vs.  $\chi$  at constant  $T$ ,  $F(V/V_0, T)$ 

$x = V/V_0$	$F(x, 300)$	$F(x, 500)$	$F(x, 1000)$	$F(x, 1500)$	$F(x, 2000)$
	(J/g)				
0.70	3830	3760	3300	2560	1630
0.72	3174	3100	2570	1820	860
0.74	2605	2520	1960	1180	180
0.76	2112	2020	1430	620	-410
0.78	1689	1580	970	130	-930
0.80	1330	1210	610	-290	-1390
0.82	1018	900	240	-660	-1780
0.84	759	630	-50	-980	-2130
0.86	543	400	-290	-1250	-2420
0.88	366	220	-500	-1480	-2680
0.90	220	70	-650	-1670	-2890
0.92	114	-50	-800	-1830	-3070
0.94	31	-140	-900	-1960	-3220
0.96	-26	-200	-990	-2060	-3350
0.98	-60	-240	-1040	-2140	-3450
1.00	-74	-260	-1080	-2200	-3530
1.02	-69	-260	-1100	-2240	-3580
1.04	-47	-250	-1100	-2260	-3620
1.06	-10	-220	-1080	-2260	-3640
1.08	40	-170	-1050	-2260	-3650
1.10	100	-120	-1000	-2230	-3650
1.12	170	-50	-950	-2200	-3630
1.14	260	30	-890	-2150	-3600
1.16	350	120	-820	-2100	-3570
1.18	450	210	-730	-2040	-3520

$$V(T^*, P = 0) = \int_{T_0}^{T^*} \alpha \, dT + V(T_0, P = 0). \quad (13)$$

To get  $V(T^*, P)$  we must account for the opposite effects of pressure and temperature on the volume. The calculation is made by adding the decrease in  $\Delta\chi$  due to pressure at absolute zero to the increase in  $\Delta\chi$  due to  $T$  at  $P = 0$ :

$$\Delta V(T^*, P) = \Delta V(T = 0, P) + \Delta V(T^*, P = 0), \quad (14)$$

where, in general,

$$\Delta V = V_0(\chi - 1).$$

$\Delta V(0, P)$  as seen later in Table 13, is found by using the Birch-Murnaghan equation of state and  $\Delta V(T^*, P = 0)$  is found from the values of  $\rho$  in Table 1.

A listing of values for  $S_p$  vs  $T$  and  $P$  as found in Table 8 is plotted in Fig. 5.

## 2.5. Enthalpy Versus Pressure and Temperature

The enthalpy versus  $T$  at  $P = 0$ ,  $H(T, 0)$ , is copied from Garvin *et al.*<sup>7</sup> and shown as the first column in Table 9.

The variation of enthalpy versus pressure at constant temperature  $T^*$  is found to be (see Appendix, Sec. 6.4.)

$$\begin{aligned} H(T^*, P) - H(T^*, 0) = & - \int_{V(T^*, 0)}^{V(T^*, P)} K_T \, dV \\ & + T^* [S(T^*, P) - S(T^*, 0)], \end{aligned} \quad (15)$$

where  $K_T$  at  $T = 0$  is found from the volume derivative of Eq. (7):

$$\begin{aligned} K_T(0, \chi) = & K_{T_0} \left( \frac{y}{y_0} \right)^{5/3} \\ & \times \left\{ 1 + \frac{1}{2} (3K'_0 - 5) \left[ \left( \frac{y}{y_0} \right)^{2/3} - 1 \right] \right\}. \end{aligned} \quad (16)$$

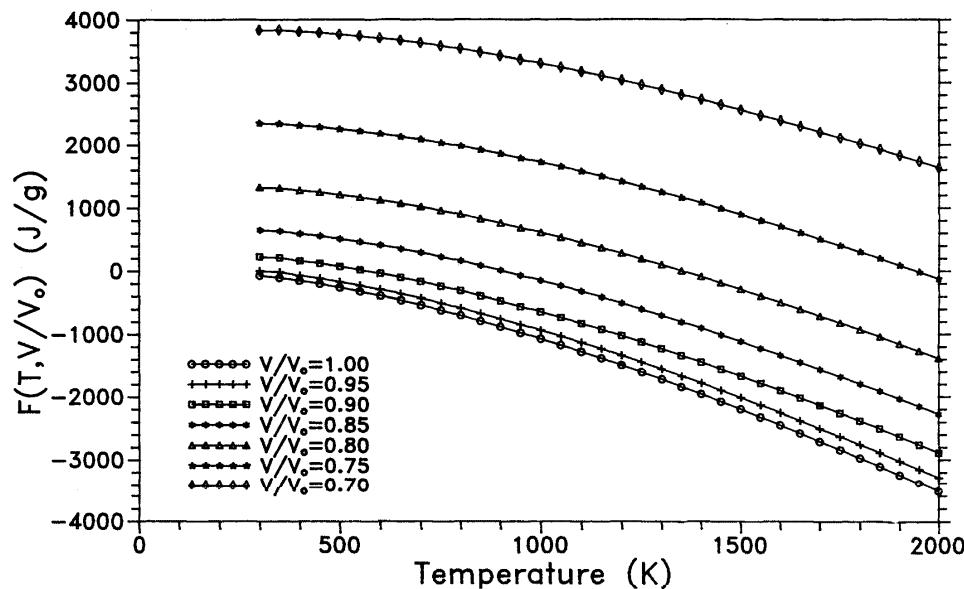
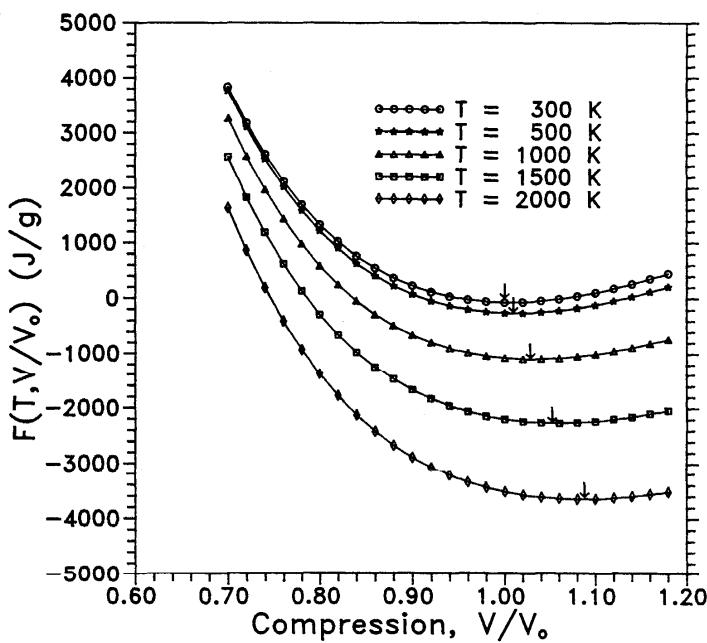
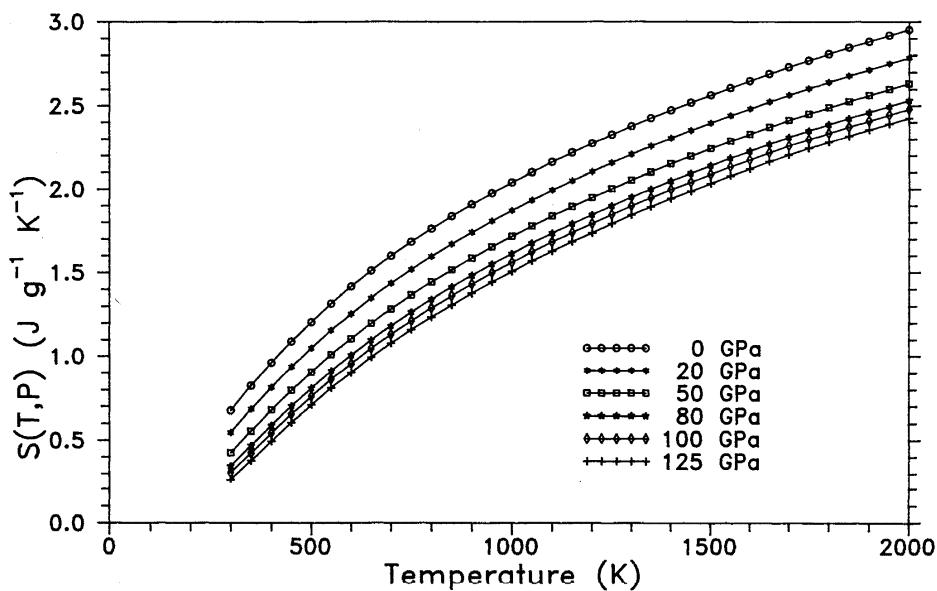
FIG. 3. The isochoric plots of Helmholtz energy  $F_v$  vs  $T$ .FIG. 4. The isothermal plots of Helmholtz energy  $F_T$  vs  $\chi$ . The arrows indicate the position of the minimum in  $F$ , which establishes the equilibrium volume at that  $T$ , relative to  $V_0$ .

Table 7. Helmholtz energy vs. T at constant  $\chi$ ,  $F(T, V/V_o)$ 

T (K)	$F(T, 1.0)$	$F(T, 0.95)$	$F(T, 0.90)$	$F(T, 0.85)$	$F(T, 0.80)$	$F(T, 0.75)$	$F(T, 0.70)$
	(J/g)						
300	-74	0	220	650	1330	2350	3830
350	-111	-19	210	630	1320	2340	3830
400	-155	-74	160	590	1280	2310	3810
450	-206	-120	120	550	1250	2290	3790
500	-263	-170	70	510	1210	2260	3760
550	-325	-230	20	460	1170	2220	3740
600	-393	-290	-40	410	1120	2180	3700
650	-465	-360	-110	350	1070	2140	3660
700	-541	-430	-170	290	1010	2090	3620
750	-622	-510	-240	220	950	2030	3580
800	-706	-590	-320	160	890	1980	3530
850	-794	-670	-400	82	820	1920	3480
900	-886	-760	-480	6	750	1850	3420
950	-980	-850	-560	-74	680	1790	3360
1000	-1080	-940	-650	-160	610	1720	3300
1050	-1180	-1040	-740	-240	530	1650	3240
1100	-1280	-1140	-840	-330	440	1570	3170
1150	-1390	-1240	-930	-420	360	1490	3100
1200	-1500	-1340	-1030	-510	270	1420	3030
1250	-1610	-1450	-1130	-610	180	1330	2960
1300	-1720	-1560	-1230	-710	93	1250	2880
1350	-1840	-1670	-1340	-810	-1	1160	2800
1400	-1960	-1780	-1450	-910	-97	1070	2720
1450	-2080	-1900	-1560	-1010	-190	980	2640
1500	-2200	-2020	-1670	-1120	-290	890	2560
1550	-2330	-2140	-1790	-1230	-400	800	2470
1600	-2450	-2260	-1900	-1340	-500	700	2390
1650	-2580	-2380	-2020	-1450	-610	600	2300
1700	-2710	-2500	-2140	-1560	-710	500	2210
1750	-2840	-2630	-2260	-1680	-820	400	2110
1800	-2980	-2760	-2380	-1800	-930	300	2020
1850	-3110	-2890	-2510	-1910	-1040	200	1920
1900	-3250	-3020	-2630	-2030	-1160	89	1830
1950	-3390	-3160	-2760	-2160	-1270	-19	1730
2000	-3530	-3290	-2890	-2280	-1390	-130	1630

Table 8. Entropy vs. T at constant P,  $S(T, P)$ 

T (K)	$S(T, 0)$	$S(T, 20)$	$S(T, 50)$	$S(T, 80)$	$S(T, 100)$	$S(T, 125)$
	(J g <sup>-1</sup> K <sup>-1</sup> )					
300	0.6743	0.54	0.42	0.35	0.31	0.26
350	0.824	0.68	0.55	0.47	0.42	0.38
400	0.962	0.81	0.68	0.59	0.54	0.49
450	1.089	0.94	0.80	0.70	0.65	0.60
500	1.207	1.05	0.91	0.81	0.76	0.71
550	1.316	1.16	1.01	0.91	0.86	0.81
600	1.417	1.26	1.11	1.01	0.96	0.90
650	1.512	1.35	1.20	1.10	1.05	0.99
700	1.600	1.44	1.28	1.18	1.13	1.08
750	1.684	1.52	1.37	1.27	1.21	1.16
800	1.762	1.60	1.44	1.34	1.29	1.24
850	1.837	1.67	1.52	1.41	1.36	1.31
900	1.908	1.74	1.59	1.48	1.43	1.38
950	1.976	1.81	1.65	1.55	1.50	1.44
1000	2.040	1.87	1.72	1.61	1.56	1.51
1050	2.102	1.93	1.78	1.68	1.62	1.57
1100	2.161	1.99	1.84	1.73	1.68	1.63
1150	2.218	2.05	1.89	1.79	1.74	1.69
1200	2.273	2.10	1.95	1.85	1.79	1.74
1250	2.325	2.16	2.00	1.90	1.85	1.79
1300	2.376	2.21	2.05	1.95	1.90	1.84
1350	2.426	2.26	2.10	2.00	1.95	1.89
1400	2.473	2.31	2.15	2.05	2.00	1.94
1450	2.519	2.35	2.20	2.09	2.04	1.99
1500	2.564	2.40	2.24	2.14	2.09	2.03
1550	2.608	2.44	2.29	2.19	2.13	2.08
1600	2.650	2.48	2.33	2.23	2.17	2.12
1650	2.691	2.52	2.37	2.27	2.22	2.16
1700	2.731	2.57	2.41	2.31	2.26	2.21
1750	2.770	2.60	2.45	2.35	2.30	2.24
1800	2.808	2.64	2.49	2.39	2.34	2.28
1850	2.846	2.68	2.53	2.42	2.37	2.32
1900	2.882	2.72	2.56	2.46	2.41	2.36
1950	2.918	2.75	2.60	2.50	2.44	2.39
2000	2.953	2.79	2.63	2.53	2.48	2.43

FIG. 5. The isobaric plots of entropy  $S_p$  at constant  $P$  vs  $T$ .

The value of  $K_{T_0}$  used is 166.2 GPa, as discussed in the Sec. 2.6. The thermal bulk modulus correction is sufficiently small compared to  $K_T$  at absolute zero to be safely ignored.

Using Eqs. (15) and (16) and values of  $H$  at  $P = 0$  from Garvin *et al.*,<sup>7</sup> values of  $H$  vs  $T$  and  $P$  are found from Eq. (15) and listed in Table 9. The isotherms are listed in Table 10. The isobars of  $H$  vs  $T$  are shown in Fig. 6, and the isotherms of  $H$  vs  $P$  are shown in Fig. 7.

An alternative derivation is to use the general formula

$$H = U + PV,$$

but  $U$  must be made over into a function of  $P$  and  $T$  (see Appendix, Sec. 6.4.).

## 2.6. The Gibbs Energy Versus Pressure and Temperature

We use

$$G(T, P) = H(T, P) - TS_p(T, P) \quad (17)$$

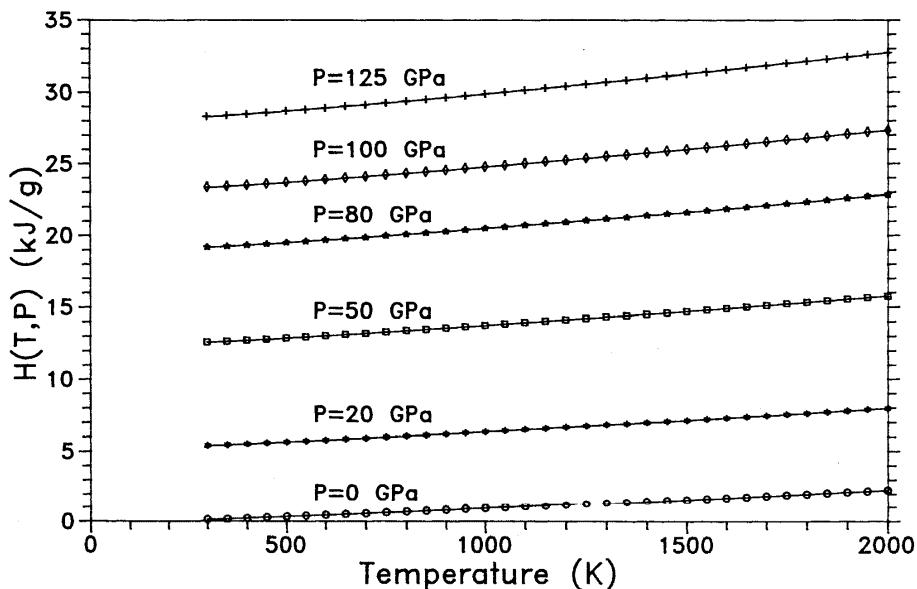
to find values of the Gibbs energy. Listing of  $G$  vs  $T$  and  $P$  is found in Table 11. The isobars of  $G$  vs  $T$  are found in Fig. 8.

Table 9. Enthalpy vs.  $T$  at constant  $P$ ,  $H(T, P)$ 

T (K)	$H(T, 0)$	$H(T, 20)$	$H(T, 50)$	$H(T, 80)$	$H(T, 100)$	$H(T, 125)$
300	0.1297	5.41	12.6	19.2	23.3	28.3
350	0.1782	5.46	12.6	19.2	23.4	28.4
400	0.2300	5.52	12.7	19.3	23.5	28.5
450	0.2841	5.58	12.8	19.4	23.6	28.6
500	0.3397	5.64	12.9	19.5	23.7	28.7
550	0.3970	5.71	13.0	19.6	23.8	28.8
600	0.4552	5.78	13.0	19.7	23.9	28.9
650	0.5143	5.85	13.1	19.8	24.0	29.0
700	0.5741	5.92	13.2	19.9	24.1	29.1
750	0.6346	5.99	13.3	20.0	24.2	29.3
800	0.6957	6.06	13.4	20.1	24.3	29.4
850	0.7573	6.13	13.5	20.2	24.4	29.5
900	0.8194	6.21	13.6	20.3	24.5	29.6
950	0.8819	6.28	13.6	20.4	24.6	29.7
1000	0.9448	6.36	13.7	20.5	24.8	29.9
1050	1.008	6.43	13.8	20.6	24.9	30.0
1100	1.072	6.51	13.9	20.7	25.0	30.1
1150	1.136	6.58	14.0	20.8	25.1	30.3
1200	1.200	6.66	14.1	20.9	25.2	30.4
1250	1.265	6.74	14.2	21.0	25.4	30.5
1300	1.329	6.82	14.3	21.2	25.5	30.7
1350	1.395	6.90	14.4	21.3	25.6	30.8
1400	1.460	6.98	14.5	21.4	25.7	31.0
1450	1.526	7.06	14.6	21.5	25.9	31.1
1500	1.592	7.14	14.7	21.6	26.0	31.2
1550	1.658	7.22	14.8	21.7	26.1	31.4
1600	1.725	7.30	14.9	21.9	26.3	31.5
1650	1.792	7.38	15.0	22.0	26.4	31.7
1700	1.859	7.46	15.1	22.1	26.5	31.8
1750	1.926	7.55	15.2	22.2	26.7	32.0
1800	1.994	7.63	15.3	22.3	26.8	32.1
1850	2.062	7.71	15.4	22.5	26.9	32.3
1900	2.130	7.80	15.5	22.6	27.1	32.4
1950	2.199	7.88	15.7	22.7	27.2	32.6
2000	2.268	7.97	15.8	22.8	27.3	32.7

Table 10. Enthalpy vs.  $P$  at constant  $T$ ,  $H(P, T)$ 

P (GPa)	$H(P, 300)$	$H(P, 500)$	$H(P, 1000)$	$H(P, 1500)$	$H(P, 2000)$
0	0.1297	0.3397	0.9448	1.5918	2.268
5	1.50	1.72	2.3	3.0	3.8
10	2.83	3.05	3.7	4.4	5.2
15	4.13	4.36	5.0	5.8	6.6
20	5.41	5.64	6.3	7.1	8.0
25	6.66	6.90	7.6	8.5	9.3
30	7.88	8.13	8.9	9.7	10.6
35	9.09	9.35	10.1	11.0	11.9
40	10.3	10.5	11.3	12.2	13.2
45	11.4	11.7	12.5	13.5	14.5
50	12.6	12.9	13.7	14.7	15.8
55	13.7	14.0	14.9	15.9	16.9
60	14.8	15.1	16.0	17.1	18.2
65	16.0	16.3	17.2	18.2	19.4
70	17.0	17.3	18.3	19.4	20.5
75	18.1	18.4	19.4	20.5	21.7
80	19.2	19.5	20.5	21.6	22.8
85	20.2	20.6	21.5	22.7	24.0
90	21.3	21.6	22.6	23.8	25.1
95	22.3	22.6	23.7	24.9	26.2
100	23.3	23.7	24.8	26.0	27.3
105	24.4	24.7	25.8	27.1	28.4
110	25.3	25.7	26.8	28.1	29.5
115	26.4	26.7	27.8	29.2	30.6
120	27.4	27.7	28.9	30.2	31.7
125	28.3	28.7	29.9	31.2	32.7

FIG. 6. The isobaric plots of enthalpy  $H_P$  at constant  $P$  vs  $T$ 

### 2.7. Evidence for the Quasiharmonic Model for MgO out to 2000 K

The variation of  $C_P$  with  $T$  at constant pressure ( $P = 1$  atmosphere) and the computed  $C_V$  at constant volume ( $\chi = 1$ ) with  $T$ , as well as the variation of entropy, both  $S_P$  and  $S_\chi$  ( $P = 1$  atmosphere;  $\chi = 1$ ), are shown in Fig. 9. We find  $C_V$  to be classical with little evidence of anharmonicity in our temperature range. That is,  $(\partial C_V / \partial T)_P = 0$ , indicating that in the density of states the frequencies are a function of  $V$  but not of  $T$  at least up to about 2000 K.

## 3. The Strategy of the Calculations

### 3.1. Zero Pressure Data

In general we followed the principle of the method of computing thermodynamic functions outlined by Slater.<sup>12</sup> Laboratory data on  $\alpha$ ,  $C_P$ ,  $K_S$ , and  $(\partial K_S / \partial T)_P$  were each represented by polynomials, and data for each of the quantities was computed at 10 degree temperature intervals from 300 to 2000 K and then stored in a database. Then,  $\gamma$ ,  $\delta_T$ ,  $C_V$ , and  $\alpha K_T$  were computed at 10 degree temperature intervals and stored, and the following were computed

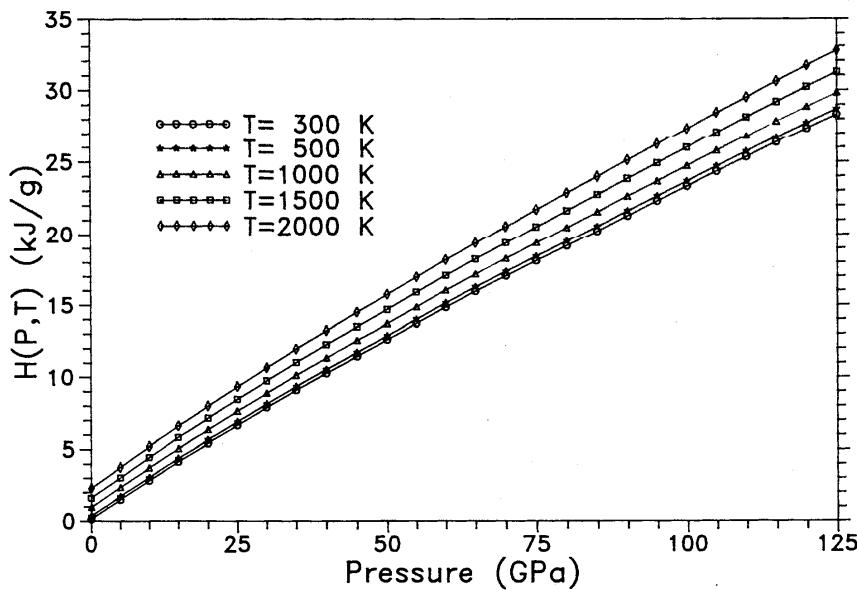
FIG. 7 The isothermal plots of enthalpy  $H_P$  at constant  $T$  vs  $P$ .

Table 11. The Gibbs energy vs.  $T$  at constant  $P$ ,  $G(T,P)$ 

$T$ (K)	$G(T,0)$ (kJ/g)	$G(T,20)$ (kJ/g)	$G(T,50)$ (kJ/g)	$G(T,80)$ (kJ/g)	$G(T,100)$ (kJ/g)	$G(T,125)$ (kJ/g)
300	-0.0726	5.24	12.5	19.1	23.2	28.2
350	-0.1101	5.22	12.5	19.1	23.3	28.3
400	-0.1547	5.19	12.4	19.1	23.3	28.3
450	-0.2060	5.16	12.4	19.1	23.3	28.3
500	-0.2635	5.12	12.4	19.1	23.3	28.3
550	-0.3266	5.07	12.4	19.1	23.3	28.3
600	-0.3949	5.02	12.4	19.1	23.3	28.4
650	-0.4682	4.97	12.3	19.1	23.3	28.4
700	-0.5459	4.91	12.3	19.0	23.3	28.4
750	-0.6280	4.85	12.3	19.0	23.3	28.4
800	-0.7142	4.78	12.2	19.0	23.3	28.4
850	-0.8042	4.71	12.2	19.0	23.3	28.4
900	-0.8978	4.64	12.1	18.9	23.2	28.4
950	-0.9950	4.56	12.1	18.9	23.2	28.4
1000	-1.095	4.48	12.0	18.9	23.2	28.4
1050	-1.199	4.40	12.0	18.8	23.2	28.4
1100	-1.306	4.32	11.9	18.8	23.2	28.3
1150	-1.415	4.23	11.8	18.8	23.1	28.3
1200	-1.527	4.14	11.8	18.7	23.1	28.3
1250	-1.642	4.04	11.7	18.7	23.1	28.3
1300	-1.760	3.95	11.6	18.6	23.0	28.3
1350	-1.880	3.85	11.6	18.6	23.0	28.3
1400	-2.002	3.75	11.5	18.5	22.9	28.2
1450	-2.127	3.65	11.4	18.5	22.9	28.2
1500	-2.254	3.54	11.4	18.4	22.9	28.2
1550	-2.384	3.44	11.3	18.4	22.8	28.2
1600	-2.515	3.33	11.2	18.3	22.8	28.1
1650	-2.649	3.22	11.1	18.2	22.7	28.1
1700	-2.784	3.10	11.0	18.2	22.7	28.1
1750	-2.922	2.99	10.9	18.1	22.6	28.0
1800	-3.061	2.87	10.9	18.0	22.6	28.0
1850	-3.202	2.76	10.8	18.0	22.5	28.0
1900	-3.346	2.64	10.7	17.9	22.5	27.9
1950	-3.491	2.52	10.6	17.8	22.4	27.9
2000	-3.637	2.39	10.5	17.8	22.4	27.9

as a function of  $T$  and stored at 10 degree intervals:  $\int_{300}^T (C_p/T) dT$ ;  $\int_{300}^T C_p dT$ ;  $\int_{300}^T C_V dT$ ;  $\int_{300}^T (C_V/T) dT$ ;  $\delta_T = -(1/\alpha K_T)(\partial K_T/\partial T)_{P=0}$ ; and  $\delta_S = -(1/\alpha K_S) \times (\partial K_S/\partial T)_{P=0}$ .

The entropy at 300 K (a constant of integration at  $V/V_0 = 1$ ) was found by integrating  $\int_0^{300} [(C_p - C_V)/T] dT$ , and comparing this with the measured entropy at  $P = 0$  and  $T = 300$  K. The value of  $\rho/\rho_0 = 1.0127 \int_{300}^T \alpha dT$  was com-

puted from 300 to  $T$  and then stored. The values of entropy and internal energy at 300 K were both calculated for constant  $V$ . Values of constant pressure entropy and enthalpy were copied from the Garvin *et al.*<sup>7</sup> tables.

### 3.2. Compression Data at Absolute Zero

Using the values of  $K_{T_0} = 166.2$  GPa,  $K_{T_0}' = 4.07$ , and  $\rho_0 = 3.6312$  (all representing estimated values for MgO at absolute zero), the pressure was calculated for  $\chi = V/V_0$  intervals of 0.001, as shown in Table 12. The inverse calculation, values of  $\chi$  for integral change in  $P$ , is shown in Table 13.

The values of  $\int_0^P P_0 d\chi$  were calculated for insertion into the internal energy [see Eq. (12)], and listed in Table 13. The function  $\int_{V_0}^V K_T d\chi$  was evaluated for each isotherm  $T^*$ , using Eq. (21) for  $K_T(V)$  where the lower limit  $V_0$  is the volume where  $P = 0$  at temperature  $T^*$  for values of  $P$  at intervals of 5 GPa, as listed in Table 13. The values of  $\int_{V_0}^V K_T dV$ , and of  $\int_{V_0}^V P_0 dV$ , for the limits  $V_0 = V(T^*, P = 0)$  and  $V = V(T^*, P)$  were computed and stored for use in the calculations of  $U$  and  $H$ .

### 3.3. The Original Experimental Data and Probable Errors

Recent measurements<sup>9</sup> of  $K_S$  up to 1800 K confirmed the high temperature extrapolations up to 1800 K made by Sumino *et al.*<sup>5</sup> on measurements taken to 1300 K. Isaak *et al.*'s data<sup>9</sup> on  $K_T$  were used over the whole temperature range.

The values of  $C_p$ ,  $S$ , and  $H$  used in these computations were taken from the thermodynamic tables of Garvin *et al.*<sup>7</sup> Their data give  $C_p$ ,  $S$ , and  $H$  up to 2000 K. The values of  $C_p - C_V$  for MgO were tabulated by Barron *et al.*,<sup>10</sup> from which the value of  $U(300, V/V_0 = 1)$  was computed using the tabulated  $U(300, P = 0)$  value.

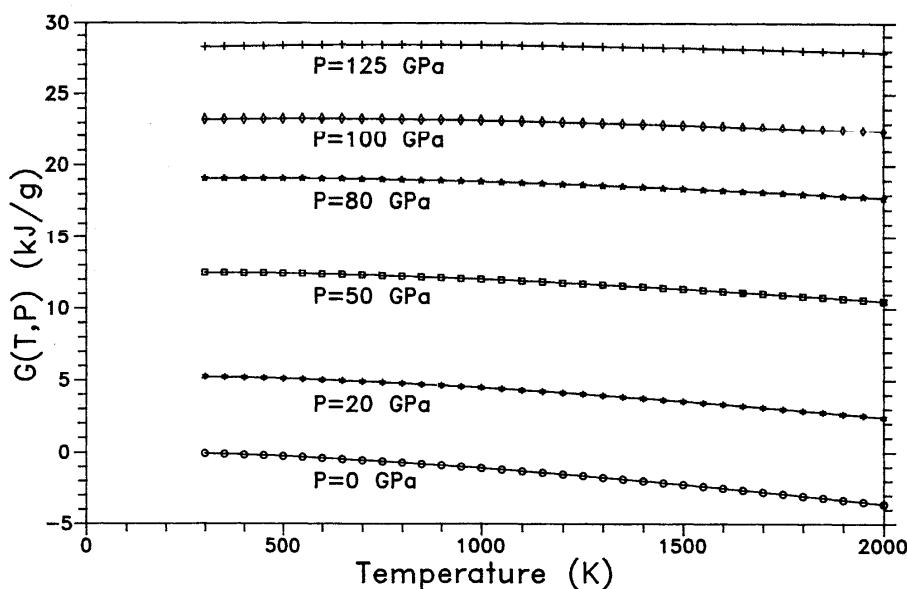
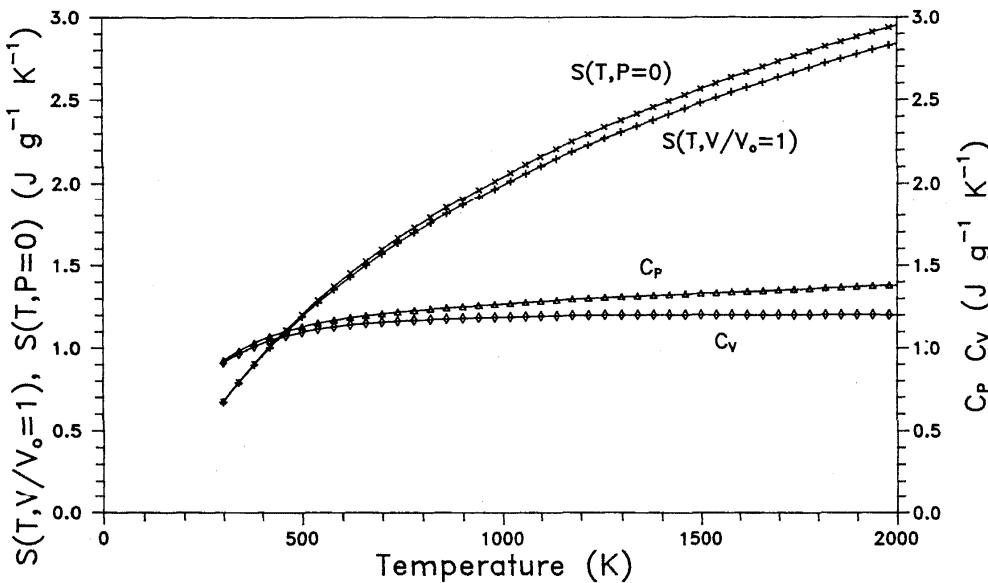


FIG. 8. The isobaric plots of Gibbs energy  $G$  at constant  $P$  vs  $T$ .

FIG. 9. Comparison of entropy at constant  $P$  and constant  $\chi$ , versus  $T$ , and the comparison of  $C_P$  and  $C_V$  vs  $T$ 

Values of  $K_T(0)$  and  $K'_T$  appropriate to absolute zero were needed, and computed as follows:

$$\frac{K_S(300)}{K_S(0)} = \left( \frac{\rho(0)}{\rho(300)} \right)^{K'_S},$$

where  $\rho(0) = 1.0127\rho(300)$ . The experiments of Jackson and Niesler<sup>13</sup> show that for MgO,  $K_S(300) = 162.5$  GPa, and  $K'_S = 4.13$ . These lead to the following values:

$$K_T(0) = 166.2 \text{ GPa}, \quad K_T(300) = 160.5 \text{ GPa},$$

$$K'_T = 4.17.$$

Transformations above from the adiabatic to isothermal bulk modulus pressure derivative use the following (see Spetzler *et al.*<sup>14</sup>):

$$K'_T = K'_S (1 + \alpha\gamma T)^{-1}$$

$$- \frac{K_S T}{(1 + \alpha\gamma T^2)} \left( \gamma \frac{\partial \alpha}{\partial P} \Big|_T + \alpha \frac{\partial \gamma}{\partial P} \Big|_T \right).$$

Table 12 The pressure and the function  $\int_P^\infty \chi dP$  vs  $\chi$ 

$x = V/V_o$	$P(V/V_o)$ (GPa)	$\int_x^\infty P d(V/V_o)$ (GPa)	$x = V/V_o$	$P(V/V_o)$ (GPa)	$\int_x^\infty P d(V/V_o)$ (GPa)
1.105	-13.4800	0.7709	0.890	24.7070	1.2293
1.100	-12.9894	0.7047	0.885	26.2091	1.3566
1.095	-12.4861	0.6410	0.880	27.7522	1.4914
1.090	-11.9697	0.5799	0.875	29.3372	1.6341
1.085	-11.4398	0.5214	0.870	30.9665	1.7848
1.080	-10.8962	0.4655	0.865	32.6402	1.9431
1.075	-10.3384	0.4124	0.860	34.3603	2.1111
1.070	-9.7663	0.3622	0.855	36.1283	2.2872
1.065	-9.1791	0.3148	0.850	37.9453	2.4723
1.060	-8.5767	0.2704	0.845	39.8126	2.6666
1.055	-7.9586	0.2291	0.840	41.7326	2.8704
1.050	-7.3245	0.1909	0.835	43.7065	3.0839
1.045	-6.6739	0.1559	0.830	45.7357	3.3074
1.040	-6.0063	0.1242	0.825	47.8222	3.5412
1.035	-5.3214	0.0959	0.820	49.9680	3.7856
1.030	-4.6186	0.0710	0.815	52.1746	4.0409
1.025	-3.8976	0.0497	0.810	54.4444	4.3074
1.020	-3.1577	0.0321	0.805	56.7793	4.5855
1.015	-2.3985	0.0182	0.800	59.1812	4.8754
1.010	-1.6195	0.0081	0.795	61.6522	5.1775
1.005	-0.8201	0.0021	0.790	64.1949	5.4921
1.000	0.0000	0.0000	0.785	66.8121	5.8197
0.995	0.8418	0.0021	0.780	69.5049	6.1605
0.990	1.7054	0.0084	0.775	72.2769	6.5150
0.985	2.5922	0.0191	0.770	75.1304	6.8836
0.980	3.5019	0.0343	0.765	78.0684	7.2666
0.975	4.4356	0.0542	0.760	81.0934	7.6646
0.970	5.3939	0.0788	0.755	84.2082	8.0779
0.965	6.3774	0.1082	0.750	87.4168	8.5070
0.960	7.3871	0.1427	0.745	90.7217	8.9523
0.955	8.4236	0.1823	0.740	94.1260	9.4144
0.950	9.4873	0.2271	0.735	97.6336	9.8938
0.945	10.5792	0.2774	0.730	101.2482	10.3909
0.940	11.7004	0.3331	0.725	104.9734	10.9064
0.935	12.8516	0.3946	0.720	108.8132	11.4407
0.930	14.0334	0.4619	0.715	112.7713	11.9946
0.925	15.2468	0.5351	0.710	116.8524	12.5685
0.920	16.4925	0.6145	0.705	121.0608	13.1631
0.915	17.7723	0.7002	0.700	125.4013	13.7791
0.910	19.0861	0.7924	0.695	129.8786	14.4171
0.905	20.4353	0.8812	0.690	134.4976	15.0780
0.900	21.8212	0.9968	0.685	139.2634	15.7623
0.895	23.2446	1.1095	0.680	144.1823	16.4710

Table 13 The compression,  $x = V/V_o$ , and the functions  $\int_x^\infty \chi dP$  and  $\int_x^\infty P dx$  vs  $P$ 

$P$ (GPa)	$x = V/V_o$	$\int_x^\infty \chi dP$ (GPa)	$\int_x^\infty P dx$ (GPa)
0	1.000	0 0000	0 0000
5	0.972	4 9284	0 0684
10	0.948	9 7261	0 2466
15	0.926	14 4090	0 5200
20	0.907	18 9896	0 8509
25	0.889	23 4779	1 2542
30	0.873	27 8822	1 6934
35	0.858	32 2095	2 1805
40	0.845	36 4658	2 6666
45	0.832	40 6561	3 2168
50	0.820	44 7850	3 7856
55	0.809	48 8565	4 3621
60	0.798	52 8739	4 9948
65	0.788	56 8405	5 6216
70	0.779	60 7591	6 2303
75	0.770	64 6321	6 8836
80	0.762	68 4619	7 5036
85	0.754	72 2505	8 1624
90	0.746	75 9999	8 8619
95	0.739	79 7118	9 5089
100	0.732	83 3877	10 1899
105	0.725	87 0292	10 9064
110	0.719	90 6377	11 5500
115	0.712	94 2145	12 3365
120	0.706	97 7606	13 0425
125	0.701	101 2773	13 6542
130	0.695	104 7655	14 4172

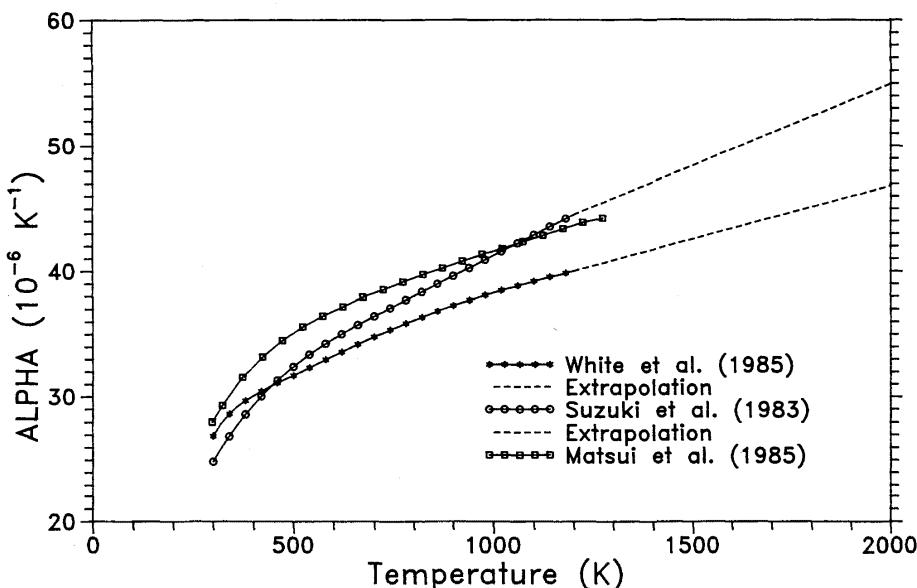


FIG. 10 The volume thermal expansivity  $\alpha$  of  $Mg_2SiO_4$ , according to three experimentalists: Suzuki *et al.*<sup>15</sup> White *et al.*<sup>16</sup> and Matsui and Manghnani<sup>17</sup>; data taken to 1200–1300 K, extrapolations of the upper and lower cases taken to 2000 K.

From this equation we get

$$K'_T = (1 + \alpha\gamma T)^{-1} [K'_S + \alpha\gamma T(\delta_T + q)], \quad (18)$$

where

$$\delta_T = -K_T \frac{\partial \ln \alpha}{\partial P} \Big|_T, \quad q = \frac{\partial \ln \gamma}{\partial \ln V} \Big|_T = -\left(\frac{\rho}{\gamma}\right) \frac{\partial \gamma}{\partial P} \Big|_T,$$

$$K_T = K_S (1 + \alpha\gamma T)^{-1}.$$

Analysis<sup>9</sup> of the measurements shows that  $\delta_T = 5.48$  for  $MgO$ , and  $q = d \ln \gamma / d \ln V = 1.5$ . Thus we find from Eq. (23) that  $K'_T$  changes from 4.13 at 300 K to 4.17 at 0 K, which is used in Eqs. (7) and (16).

Of importance to the calculation of the thermodynamic functions is the parameter  $w$  given by Eq. (2);  $w = (\partial K_T / \partial T)_V$ . In general this is a small number compared to  $(\partial K_T / \partial T)_P$  (see Table 2), but for some solids it may be temperature dependent. Its  $P=0$  value is computed from the measurements given by the balance between  $(\partial K_T / \partial T)_P$  and  $\alpha K_T (\partial K_T / \partial P)_T$ , the first term being negative and the second positive. If  $(\partial K_T / \partial T)_V$  is zero, making Eq. (2) zero, than we know from a thermodynamic identity that  $(\partial \alpha K_T / \partial V)_T$  is zero. But in general Eq. (2) is not zero, although it is often a small quantity. Also of importance is the value of the temperature dependence of  $(\partial K_T / \partial P)_T$ , or  $(d^2 K_T / d P d T)$ . For  $MgO$ , Spetzler<sup>14</sup> found  $d^2 K_T / d T d P = 0$  up to 800 K. We assumed this continued up to 2000 K.

For  $MgO$  we find that  $w$  is in the range 2–10 MPa/K, or less than 1% of the value of  $(\partial K_T / \partial T)_P$ , and it is negative. This means that the error arising from  $w$  is negligible, even if  $(\partial K_T / \partial P)_T$  turns out to be a function of  $T$  at high pressure.

The most serious uncertainty in the application of the equations presented in this paper to other solids arises from the uncertainty in the thermal expansivity at high  $T$ . The

situation on the agreement on  $\alpha$  is not bad for  $MgO$ , and so uncertainty in  $\alpha$  does not affect these results. But the thermal expansivity reports on  $Mg_2SiO_4$ , for example, illustrate that in general there is a problem in applying these equations to other solids at high temperature.

The data for high-temperature thermal expansivity of  $Mg_2SiO_4$  are shown in Fig. 10 for these experimentalists: Suzuki *et al.*<sup>15</sup>; White *et al.*<sup>16</sup>; and Matsui and Manghnani.<sup>17</sup> As can be seen the extrapolations of these three thermal expansivities lead to quite differing values of  $\alpha$  at 2000 K. This would lead to uncertainty in  $\gamma$ ,  $\alpha K_T$ , and entropy. The most serious problem in evaluating the thermodynamic functions in the high-temperature regime (near 2000 K) is the dearth of information on  $\alpha$  in this region. In general, an error of 20% in  $\alpha$  at 2000 K, as shown in Fig. 10, would lead to a 7% error in entropy at  $\chi = 0.7$  and  $T = 2000$  K, but to virtually no error at  $\chi = 1$ . An error of 20% in  $\alpha$  at 2000 K would lead to about 1% error in  $U$  and  $H$ , since these functions are dominated by the integrals of the equation of state, and  $\alpha$  affects only the density.

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